INVESTIGATION OF HYSTERESIS AND RELAXATION BEHAVIOUR IN GRAPHITE AND $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ ELECTRODES

Muhammad Rashid[1]*, Tanveerkhan S. Pathan[2], Andrew McGordon[1], Emma Kendrick[1,2] and W. D. Widanage[1]

*Corresponding author email: R.muhammad.1@warwick.ac.uk
[1]WMG, University of Warwick, Coventry, UK, CV47AL
[2]School of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham, UK, B15 2TT

Abstract

Li-ion battery electrode materials exhibit hysteresis between lithiation and delithiation due to different thermodynamic equilibria at the same state of charge (SOC). The acquisition time for the open circuit potential (OCP) and the hysteresis behaviour of graphite and $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC) has been investigated using galvanostatic intermittent titration technique in Lithium metal anode cells. The OCP at various stages of relaxation after each current pulse have been recorded during lithiation and delithiation. The voltage hysteresis is the difference between the potential at equilibrium after lithiation and delithiation. Hysteresis is ~600 and ~300 mV below 0.1 SOC for graphite and NMC electrodes respectively, above 0.1 SOC the hysteresis is much lower 35-33 and 45-42 mV, with short rest requirements of 5-120 min. The error in hysteresis voltage with shorter relaxation times is compared to 120 min rest. This analysis shows that 5 min. has an error of 16 mV for graphite and 2 mV for NMC between 0.1-1 SOC. Below 0.1 SOC, 90 min. (for graphite/NMC) and between 0.1-1 SOC, 30 min. (for graphite) and 5 min. (for NMC) at charge rates below C/20 are appropriate relaxation times and can shorten the OCP parameter acquisition test time significantly.

Keywords

OCP; hysteresis; relaxation; experimental duration; GITT

1. Introduction

Li-ion battery parameters are required to model the electrochemical processes taking place inside the battery. There are several variables/parameters governing the battery state of charge (SOC), output voltage and capacity. Open circuit potential (OCP) is one of the most important input variables to estimate the instantaneous cell voltage using numerical models [1]. However, OCP has a significant hysteresis which corresponds to the different thermodynamic equilibria

of the material under charging and discharging processes [2-4]. The hysteresis in OCP varies with SOC which needs to be considered in battery modelling [5]. Several studies to elucidate the hysteresis in open circuit potential of the Li-ion batteries are reported [2-5]. Dreyer *et al.* [2] explained the thermodynamic view point of having different equilibrium potential during the lithiation and delithiation for the same SOC of the electrode. Barai *el al.* [3] investigated the hysteresis of cylindrical and pouch cells with various rated capacities and cell chemistries. Another study investigated the difference in equilibrium potential of $LiFePO_4$/Graphite cells and reported the different hysteresis voltages with SOCs [4]. These studies have been carried out on commercial full-cells where the computed hysteresis is the compound effect of the hysteresis in the individual electrodes. For precise battery monitoring/control using mathematical models, the SOC dependent OCP and the hysteresis of each electrode need to be gauged [4-9]. The time for the OCP parameter acquisitions can be long (2 weeks), and therefore OCP has been estimated in some cases as the mid voltage between charge and discharge. This practice doesn't take into consideration the voltage hysteresis observed between charge and discharge, and in addition has polarization effects particularly below 10% SOC which are not observed at steady state.

To obtain the OCP of the electrodes various studies have been conducted using galvanostatic intermittent titration technique (GITT) at different currents (C/10-C/50), pulse durations (10-60 min.) and relaxation durations (15-600 min.) [10-17]. However, very few studies have been conducted on the OCP hysteresis of the individual electrodes [6,11]. Farkhondeh *et al.* [6] have computed a voltage hysteresis of 8 mV for the $LiFePO_4$ and Croy et al. [11] have observed the varying voltage hysteresis with SOC of the Ni and Mn based composite cathode. GITT is usually used with short current pulses and long arbitrary relaxation times to ensure that OCP has been reached, this leads to long test times. Too short a rest duration results in a non-steady state OCP, with lithium concentration gradients between the electrode solid matrix and further

relaxation required to reach equilibrium voltage. Longer relaxation duration results in increased test durations and cost. To date, no investigations have been carried out to investigate the effect of rest duration on the OCP measurement of the battery electrodes and the change in rate of voltage drop at different SOC.

The objectives of the present study have been directed towards the quantification of the OCP relaxation for graphite and $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC) electrodes using in-house assembled coin-cells in half-cell format. The voltage rate of change during relaxation to OCP is analysed at different SOC's. This study reveals the sensitive SOC zone for the electrode OCPs and the corresponding relaxation time for future model parameterization. This study investigates the tradeoff between the experimental duration and the corresponding accuracy required to guide researchers in selecting the relaxation duration for OCP measurements.

2. Methodology

Electrode slurry was prepared with a composition of Graphite: Carbon Black (CB): poly-vinylidesflouride (PVDF) in proportion of 92:2:6 [18,19] for anode and NMC: CB: PVDF in proportion of 92:5:3 [18,19] for cathode in N-methyl-2-pyrrolidone. The slurries were coated on copper and aluminum foil for anode and cathode, respectively, and subsequently dried over a hot plate at 90°C for 30 min. and overnight in a vacuum oven at 45°C. Thereafter, coated sheets were calendared up to 30-40% of porosity and circular disks of diameter 1.5 cm were cut. The cut disks were used to assemble 2032 type coin-cells with a lithium metal anode. A 20 μm thick polyethylene film of diameter 1.9 cm used as a separator. The electrolyte used was 1M $LiPF_6$ in EC/EMC 3/7(v/v) + 1%wt. VC, as previously described [20].

Two Li-graphite and Li-NMC cells were assembled and subjected to a formation process of 2 cycles between 0.005-3V [19] and 2.6-4.35V [18-19], respectively, at C/20 currents. The experimental cells and the experimental setup used in this study have been represented in Figs.

S1-S2 in supplementary materials. Afterwards, GITT was performed with consecutive current pulses and relaxation durations. The applied current pulse was C/20 for 10 min. to adjust the SOCs of the electrodes followed by 2 hour relaxation to attain an equilibrium state. The voltage limits for the GITT test are 0.005-3V and 2.6-4.35V for the graphite and NMC half-cells, respectively. The voltage change for graphite and NMC vs Li/Li+ was recorded over the relaxation period, and the time to reach OCP for the various SOCs are shown.

3. Results and Discussion

GITT was performed during lithiation and delithiation for a set of two half-cells of Li-NMC and Li-Graphite, and their voltage response analysed over a 120 min rest period. After 120 min negligible change in voltage is observed, and we therefore assume the relaxation time is sufficient for equilibrium OCP, and consequently the hysteresis evaluation over complete SOC range. The OCPs during lithiation and delithiation and their hysteresis for each of the cells have been compared in Fig. 1. Fig 1(a) shows that the lithiation OCP for the two Li-Graphite cells are nearly overlapping for the entire range of the SOC. However, the delithiation OCP for the two cells has significant variation between 0-0.13 SOC and around 0.2 SOC (0.014V) due to the microstructural and porosity differences between two graphite electrodes (see supplementary material). Above 0.23 SOC the two cells have similar voltage profiles with less than 1mV variation. Furthermore, the hysteresis for the two Li-Graphite cells shows (Fig. 1(b)) a large difference between 0.02-0.13 (up to 424mV at 0.02 SOC). Above 0.13 SOC, the two cells have insignificant difference in hysteresis (within 0.5 mV) except at 0.2 SOC (up to 24 mV) and 0.53 SOC (up to 8 mV). Similarly, the lithiation and delithiation OCPs shown in Fig. 1(c) demonstrate a very good overlap (within 2 mV) and repeatable behaviour for the two Li-NMC cells for the entire range of the SOC. Furthermore, the hysteresis for the two cells is also closely matching (within ~1.5 mV) to each other for the full SOC domain (Fig 1(d)). The results

obtained for Cell 1 (of Li-Graphite and Li-NMC cells) will be discussed in the forthcoming sections.

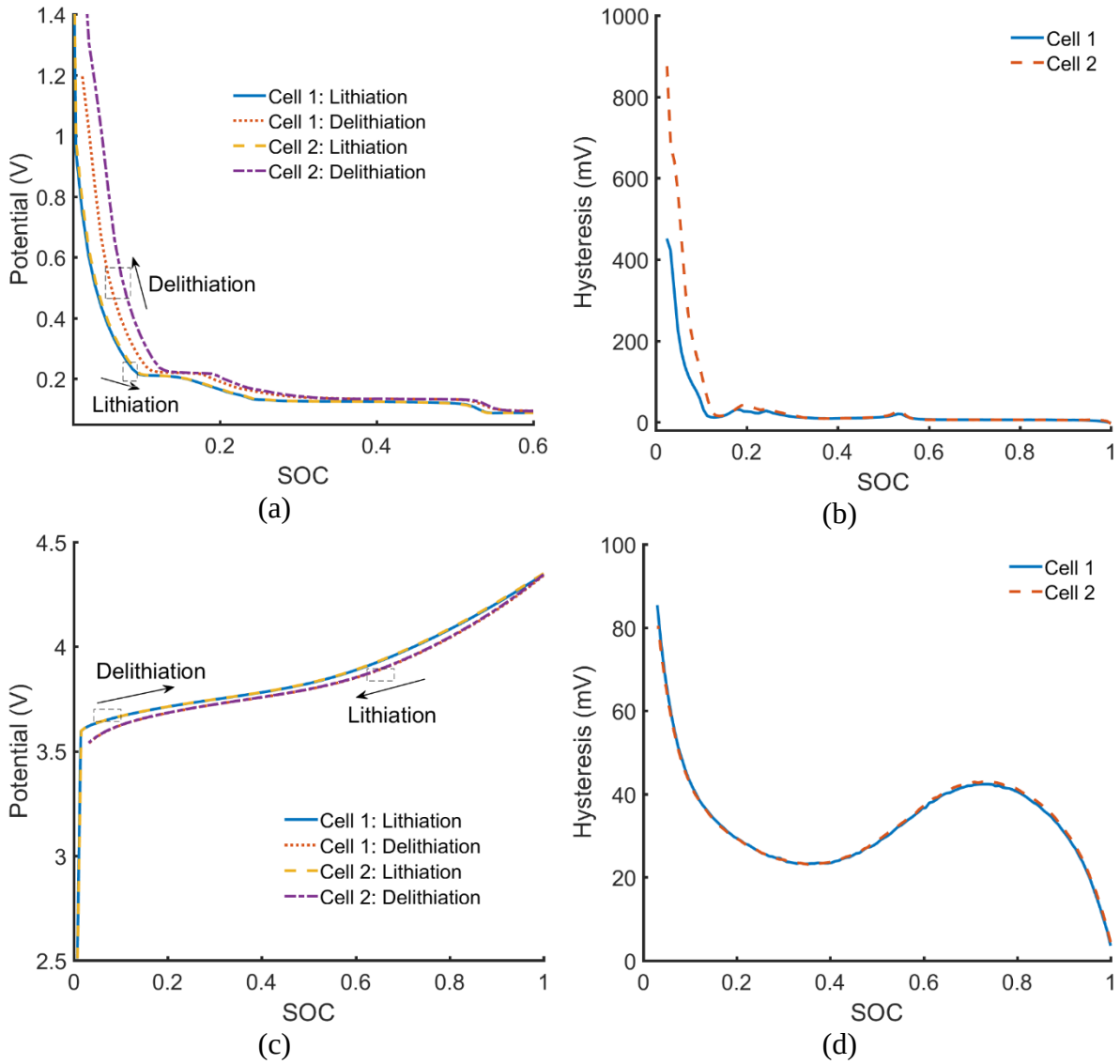


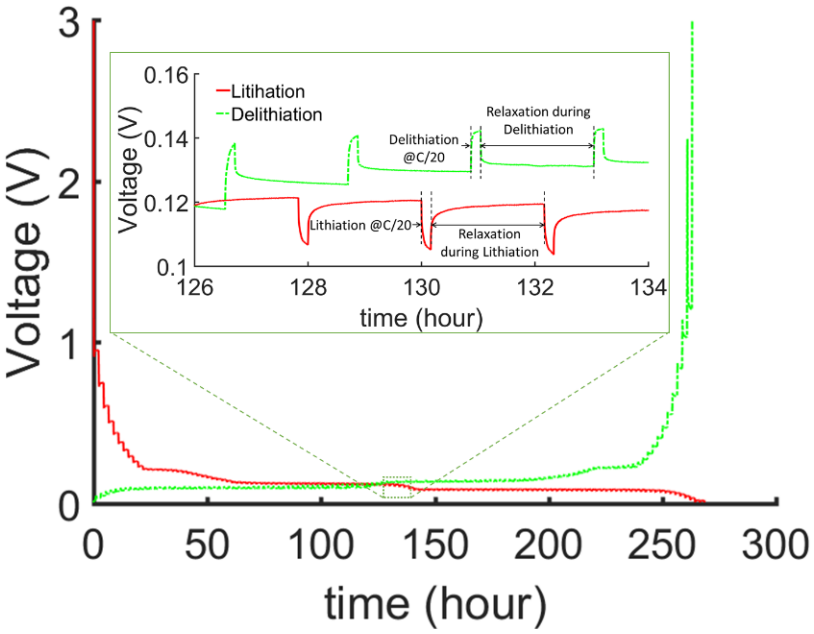
Figure 1: The comparison (a) Lithiation and delithiation OCPs and (b) Hysteresis of the two Li-Graphite cells; (c) Lithiation and delithiation OCPs and (d) Hysteresis of the two Li-NMC cells.

3.1 Graphite voltage relaxation investigation

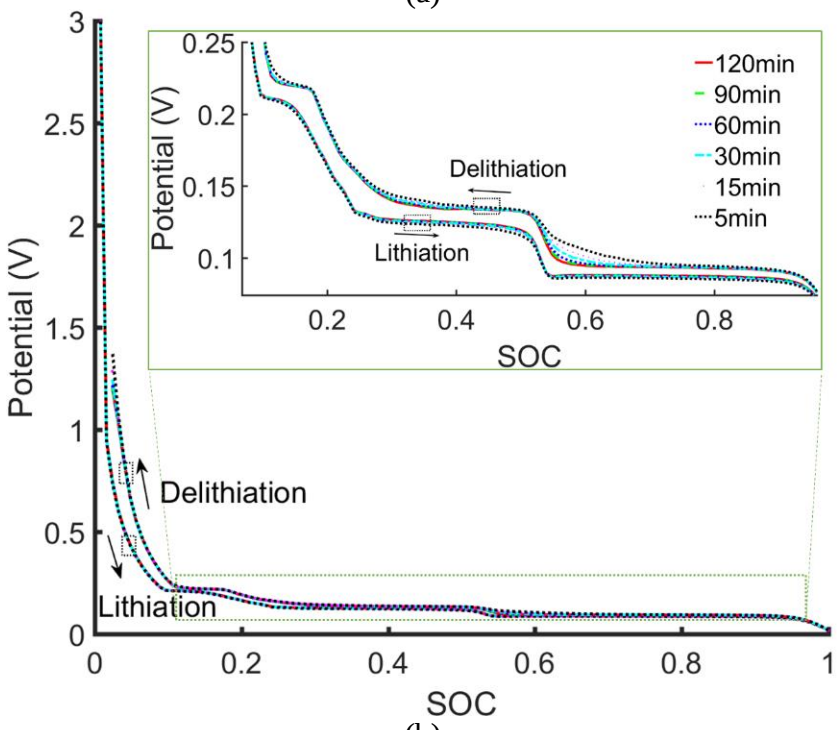
Figure 2(a) shows the lithiation and delithiation voltages, with respect to time, recorded using GITT. At the end of pulse the voltage profile relaxes to an equilibrium potential (OCP) because the lithium concentration at the surface of the active material equalising to the bulk concentration of the material. For a lithiation step, this phenomena of lithium diffusion during

relaxation, leads to higher cell voltage at the end of relaxation compared to the potential at the end of current pulse (red line in inset Fig 2(a)). During the delithiation, lithium concentration at the surface will be lower than the bulk of the electrode particle because lithium consumption at the surface take place at a faster rate as compared to lithium diffusion from the inner matrix [21]. Therefore, after removing the current pulse, lithium diffuses from the centre to the surface and leads to lower cell voltages after relaxation compared to the voltage at the end of pulse (green line in inset Fig 2(a)).

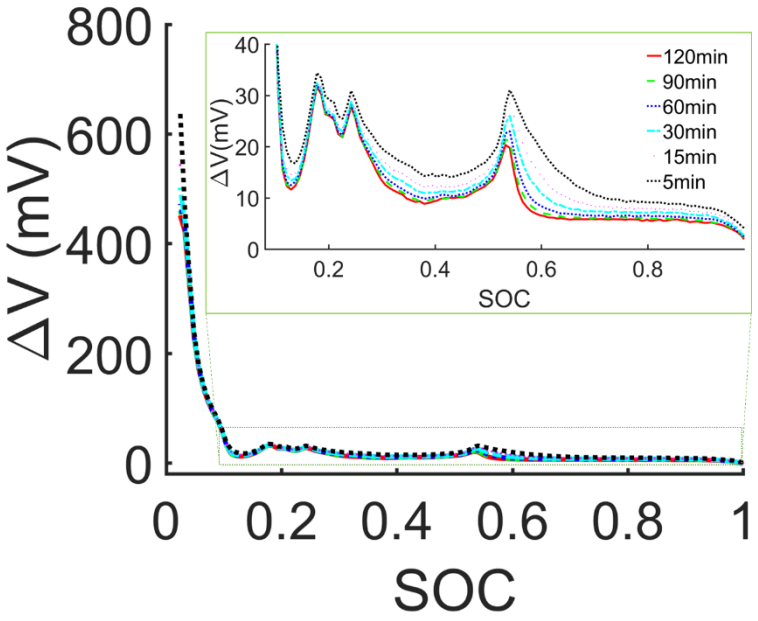
Figure 2(b) shows the Li-Graphite cell potential at different SOCs during the lithiation and delithiation at 5, 15, 30, 60, 90 and 120 min. of the relaxations. The GITT test has been conducted with 120 min. relaxation durations and the intermediate relaxation times have been used to analyze the rate of change in voltage at different SOCs. The potential vs. SOC plot in Fig. 2(b) shows the different voltage plateaus for the graphite in lithiation and delithiation. As can be seen in the inset of the Fig. 2(b), the voltage during lithiation and delithiation (for all relaxations) are not overlaying and shows the voltage change at every SOC for the voltages recorded at 5, 15, 30, 60, 90 including 120 min. relaxations. The inset of Fig. 2(b) shows that the change in voltage with longer relaxation during lithiation is insignificant for the entire SOC range while considerable change during delithiation is observed especially between 0.53-0.75 SOC.


Voltage (V)
time (hour)
Litihation
Delithiation
Delithiation @C/20
Relaxation during Delithiation
Lithiation @C/20
Relaxation during Lithiation

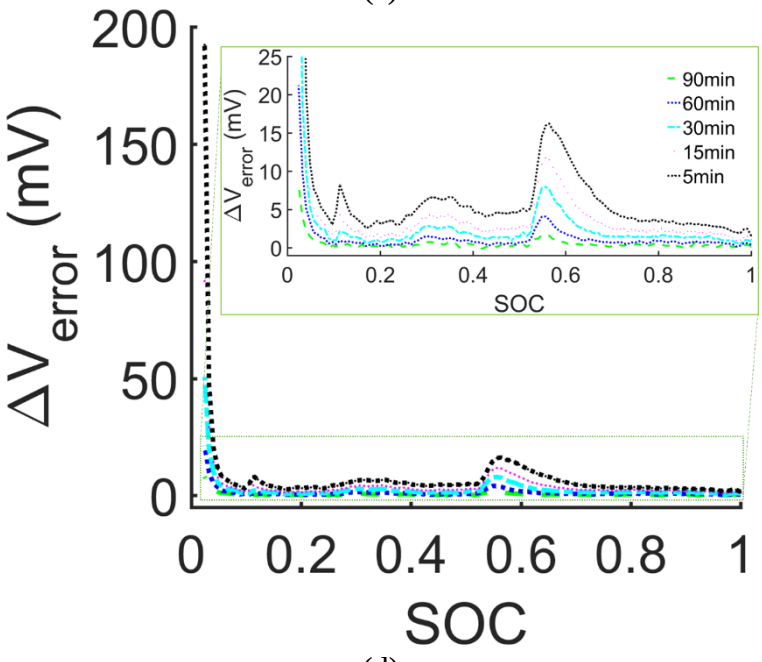
(a)


Potential (V)
SOC
120min
90min
60min
30min
15min
5min
Delithiation
Lithiation

(b)



(c)



(d)

Figure 2: (a) Cell potential vs. time for lithiation and delithiation during GITT test, (b) Equilibrium potentials at various SOCs during lithiation and delithiation, (c) Hysteresis (ΔV) between lithiation and delithiation OCPs with an enlarged view in the inset and (d) Error in voltage hysteresis (ΔV_{error})with shorter relaxation duration with respect to the 120 min. relaxation and the inset in all subplots shows the zoomed view of the same for the visual clarity.

To analyze the rate of voltage change, the difference between delithiation and lithiation voltages over relaxation time with respect to the SOC has been plotted in Fig. 2(c). The highest voltage difference (ΔV, termed as hysteresis for 120 min relaxation) is observed at 0.02 SOC,

ranging from 643-451 mV for 5-120 min. relaxations as listed in Table 1. The ΔV shows a decreasing trend as relaxation increases. At 0.02 SOC the ΔV between 5-15 min. is ~101 mV and ~92 mV for the subsequent 15-120 min. A greater change in voltage with time indicates that, at low SOC, small changes in lithium concentration lead to a significant change in voltage during lithiation and delithiation. The voltage hysteresis steeply decreases between 0.02-0.1 SOC and less than 35 mV (inset Fig. 2(c)) is observed between 0.1-1 SOC. This inset also shows that at 0.18, 0.25 and 0.53 SOCs which have ΔV of ~34, ~31 and ~28 mV for 5 min. relaxation (Table 1). However, the ΔV between 0.3-0.5 and 0.6-1 SOCs are below 15 mV (inset Fig. 2(c)) which correspond to the OCP hysteresis of the graphite between these SOCs.

Table 1: Voltage difference (ΔV) for the various stages of relaxation of graphite electrode correspond to peaks shown in Fig 2(c).

Rest (min.)↓	ΔV (mV)			
	SOC = 0.02	SOC = 0.18	SOC = 0.24	SOC = 0.53
5	643.72	34.38	30.92	27.96
15	542.97	33.24	29.42	25.96
30	502.05	32.41	28.79	24.50
60	472.67	32.06	28.28	22.61
90	459.55	31.78	28.20	21.43
120	451.44	31.67	27.85	20.32

The error in ΔV_{error} ($\Delta V_x - \Delta V_{120}$, where x = 5, 15, 30, 60 and 90 min.) has been analysed and plotted in the Fig. 2(d). The ΔV_{error} is high for low SOCs (0.02-0.06) because of the large rate of change of voltage with lithium concentration. At 0.02 SOC ΔV_{error} is 8 mV at 90 min. which decreases with SOC to less than 1 mV above 0.06 SOC. Above 0.06 SOC ΔV_{error} is 4, 8, 12, 16 mV for 60, 30, 15 and 5 min., respectively, as can be seen in inset of Fig. 2(d).

Finally, the total time required to conduct the GITT test has been analysed with various relaxation durations (Table 2). Overall 124 and 122 current pulses at C/20 have been employed to completely lithiate and delithiate the Li-Graphite cell, respectively. The total time required

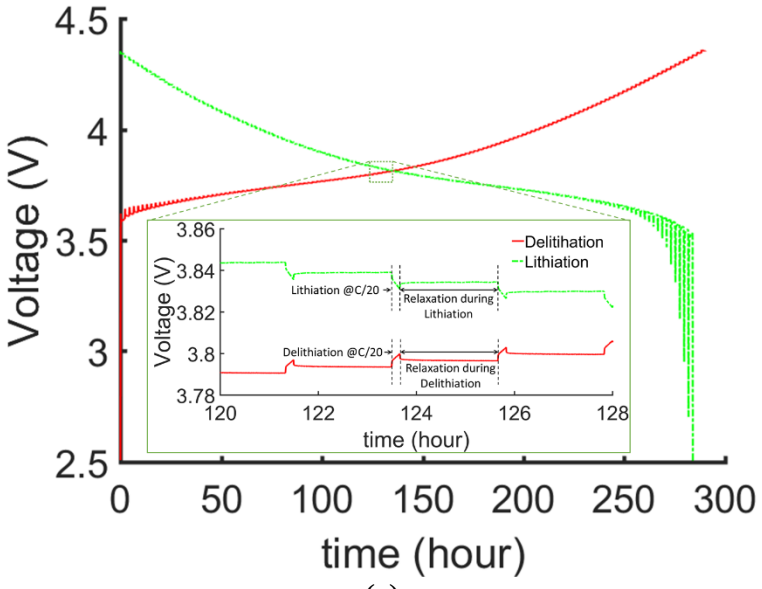
to complete the cycle with a 5 min. relaxation is ~61.5 hrs. The ΔV_{error} for 5 min. rest is below 16 mV at 0.1-1 SOC and with the full 120 min. relaxation the test taking 533 hrs. The corresponding values for 30 and 60 min. relaxation are 164 and 287 hrs. with a ΔV_{error} of 8 and 4 mV, respectively. In summary, the selection of the relaxation duration for the OCP and hysteresis measurement can be reduced whilst retaining accuracy and also reducing the time required to obtain these parameters.

Table 2: Time required to conduct the GITT test with various relaxation durations for Li-Graphite cells.

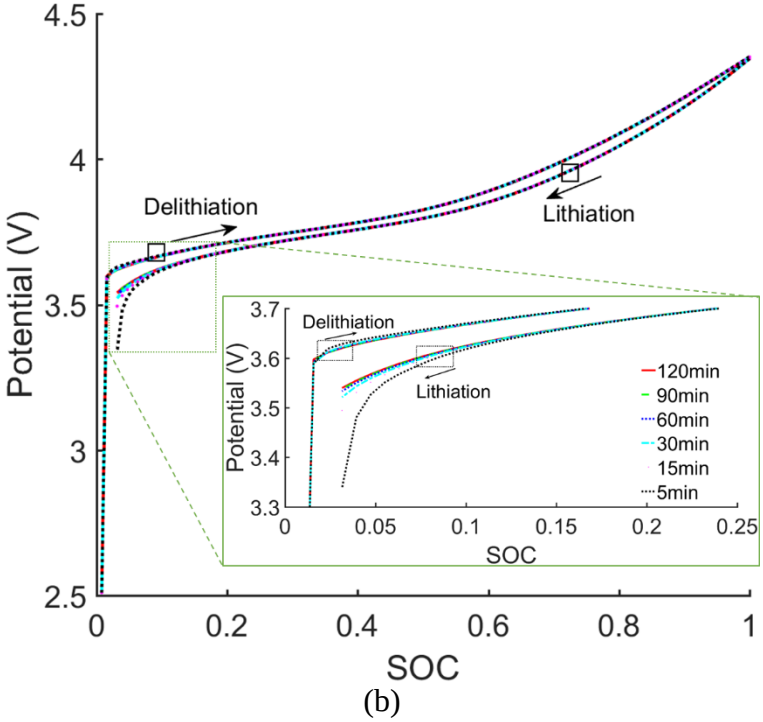
With relaxation of (min.)	5	15	30	60	90	120
Total Lithiation Relaxation time (Hrs.)	10.3	31.0	62.0	124.0	186.0	248.0
Total Lithiation Pulse time (Hrs.)	20.7	20.7	20.7	20.7	20.7	20.7
Total Lithiation time (Hrs.)	***31.0***	***51.7***	***82.7***	***144.7***	***206.7***	***268.7***
Total Delithiation Relaxation time (Hrs.)	10. 2	30.5	61.0	122.0	183.0	244.0
Total Delithiation Pulse time (Hrs.)	20.3	20.3	20.3	20.3	20.3	20.3
Total Delithiation time (Hrs.)	***30.5***	***50.8***	***81.3***	***142.3***	***203.3***	***264.3***
Total Cycle time (Hrs.)	**61.5**	**102.5**	**164.0**	**287.0**	**410.0**	**533.0**
Max. ΔV_{error} (mV) above 0.1 SOC	16	12	8	4	1	0

3.2 NMC voltage relaxation investigation

Figure 3(a) shows the delithiation and lithiation voltages with respect to time for Li-NMC between 4.35-2.5V. With delithiation the cell voltage increases and during relaxation the cell voltage decreases caused by gradient relaxation after turning off the current pulse (red line in inset Fig 3(a)). This process was repeated until the cell voltage reached the upper cut-off which was accomplished in 127 intermittent current pulses. During lithiation, the cell potential decreases with the application of current and during relaxation the cell potential increases due to concentration gradient relaxation (green line in inset Fig 3(a)). The potential profiles shown in Fig. 3(a) have been further utilised in OCP, time to reach OCP and hysteresis quantification of the NMC electrode.



(a)



(b)

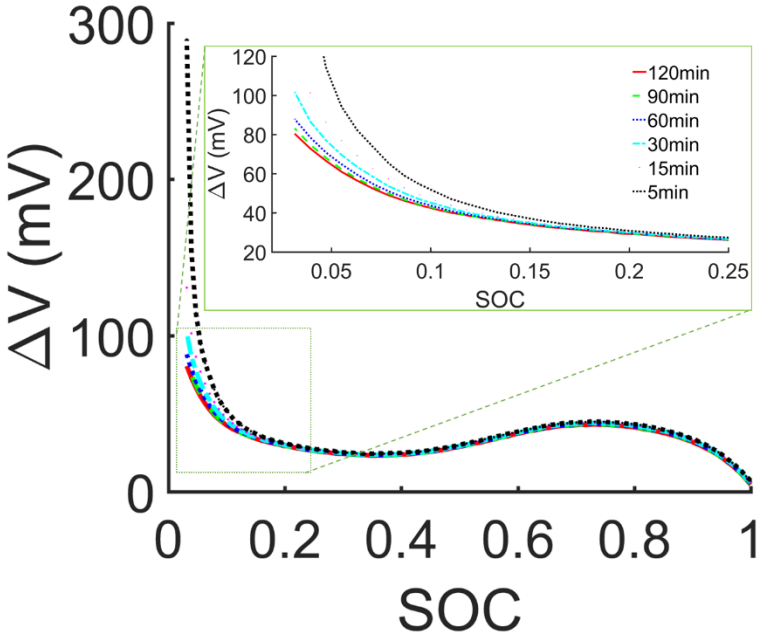
Figure 3: (a) Li-NMC Cell potential vs. time during lithiation and delithiation using GITT test which has been enlarged in the inset for the visual clarity (b) Equilibrium potentials (OCP) at various SOCs during lithiation and delithiation of Li-NMC cells and inset shows magnified view of the voltages at different relaxation stages.

The relaxation potentials after every current pulse during delithiation and lithiation of the Li-NMC cells have been extracted at 5, 15, 30, 60, 90 and 120 min. of rest and plotted in Fig 3(b) with respect to SOC. At all SOCs different voltages during lithiation and delithiation are observed at all relaxation durations, illustrating the different rates of change in voltage for NMC when charging or discharging. Similar behaviour for NMC has been reported in Lu *et al.*

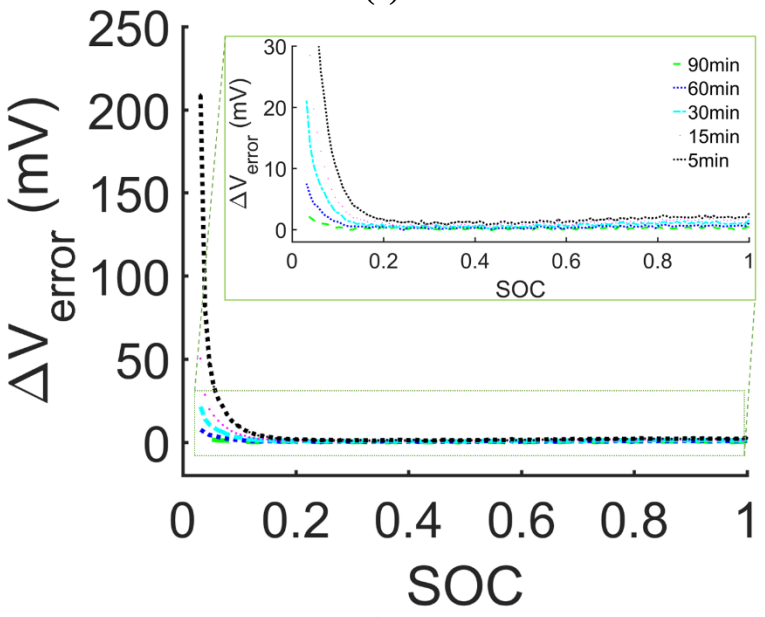
[22] who showed the voltage gap between lithiation and delithiation varies with SOC. Furthermore, the potential profile at different relaxation stages (of lithiation and delithiation) are overlapping which shows very fast gradient relaxation in the NMC solid matrix for 0.1-1 SOC. However, below 0.1 SOC the lithiation of the NMC shows a considerable change in potential with relaxation time especially below 30 min. rest (inset Fig. 3(b)) due to the slower solid phase lithium diffusivity in NMC at low SOC. In contrast, the voltage (Fig. 3(b)) at different stages of the relaxation during delithiation has insignificant change for entire range of SOC

The voltage difference from OCP (ΔV) over time between lithiation and delithiation for each SOC of the Li-NMC cell has been analysed and is shown in Fig. 4(a) for 5, 15, 30, 60, 90 and 120 min. of relaxation. As can be seen in the plot that the ΔV at 0.03 SOC are 290, 130, 101, 88, 83 and 80 mV with increasing relaxation durations, respectively. This analysis shows a large change (189 mV) in ΔV during the 5-30 min. of the relaxation compared to the successive 90 min. (21 mV) (inset Fig 4(a)) due to the high rate of change of voltage in the 0-0.1 SOC range. With rise in SOC the ΔV decreases and dropped to 25-23 mV for 5-120 min. of the relaxation time at 0.35 SOC. The further increase in the SOC leads to further rise in the ΔV can be seen in Fig 4(a). Above 0.73 SOC, the ΔV decreases with the lowest ΔV of 7-4.5 mV for 5-120 min. relaxation at the full SOC of the NMC electrode.

The ΔV_{error} for selecting shorter relaxation (5, 15, 30, 60 and 90 min.) with respect to the 120 min. rest has been computed and shown in Fig. 4(b). Highest ΔV_{error} are 210, 50, 21, 8 and 3 mV, at 0.03 SOC for the corresponding stages of relaxation, respectively. As the SOC increases the error drops down rapidly and above 0.1 SOC it stabilises below 0.3 and 0.4 mV for 60 and 90 min. rests, respectively. The ΔV_{error} above 0.2 SOC with the 5, 15 and 30 min. relaxations are below 2, 1.5 and 1 mV, respectively (inset Fig. 4(b)).



(a)



(b)

Figure 4: (a) ΔV between lithiation and delithiation OCPs at various stages of the relaxation (b) ΔV_{error} for the shorter relaxation with respect to the 120 min. relaxation of the Li-NMC cells. Both subplots have the zoomed view in the inset for the sake visual clarity.

Lastly the time span required to conduct the GITT test with these relaxation durations and corresponding percentage ΔV with respect to 120 min. relaxation have been analysed and listed in Table 3. The total time for lithiation and delithiation with a C/20 current pulse for 10 min. followed by 5 min. relaxation is 62.75 hrs. With elongated relaxation the cycle can be completed in ~167, 293 and 544 hrs. for the 30, 60 and 120 min. rest durations, respectively.

The test durations with 120 min. rest would be approximately nine times longer compared to 5 min., however, the computed ΔV in case of 5 min. are 360, 104 and 125% of the 120 min. at 0.03, 0.5 and 0.99 SOCs, respectively. The tabulated data shows that the percentage ΔV drops with a faster rate in case of early 30 min. of the relaxation compared to the following 90 min. This analysis elucidate that further increasing the relaxation has only significant reduction in ΔV at low and high SOCs (Fig 4(a)). In order to have (for example) 5% difference between observed and OPC voltage, the 10 initial and last pulses should have 30 min. relaxation, and intermediate pulses can have 5 min. relaxations which save 450 hrs. to conduct the GITT test for the Li-NMC cells.

Table 3: Time required to conduct the GITT test with various relaxation durations for Li-NMC cells.

With relaxation of (min.)		5	15	30	60	90	120
Total Lithiation Relaxation time (Hrs.)		10.6	31.8	63.5	127.0	190.5	254.0
Total Lithiation Pulse time (Hrs.)		21.2	21.2	21.2	21.2	21.2	21.2
Total Lithiation time (Hrs.)		**31.8**	**53.0**	**84.7**	**148.2**	**211.7**	**275.2**
Total Delithiation Relaxation time (Hrs.)		10.3	31.0	62.0	124.0	186.0	248.0
Total Delithiation Pulse time (Hrs.)		20.7	20.7	20.7	20.7	20.7	20.7
Total Delithiation time (Hrs.)		**31.0**	**51.7**	**82.7**	**144.7**	**206.7**	**268.7**
Total Cycle time (Hrs.)		**62.8**	**104.7**	**167.4**	**292.9**	**418.4**	**543.9**
Max. ΔV_{error} (mV) at 0.03 SOC		210	50	21	8	3	0
Percentage ΔV (against 120 min.)	SOC=0.03	360	162	126	109	103	100
	0.25	105	102	102	101	100	100
	0.50	104	103	101	100	101	100
	0.75	104	103	102	101	100	100
	0.99	125	116	112	108	104	100

4. Conclusions

In this work, the OCP, rate of change in voltage, and voltage difference to OCP with respect to time of graphite and NMC electrodes has been investigated using in-house fabricated half-cells. For this study, the GITT test has been conducted with a C/20 current pulse for 10 min. followed

by 120 min. relaxation, and the voltage at different stages of the relaxation during lithiation and delithiation have been analysed. The voltage change (ΔV) over time to OCP has been elucidated over the full SOC and voltage range for lithiation and delithiation. ΔV is shown to vary with SOC with the highest in magnitude below 0.1 SOC, for both Li-Graphite and Li-NMC, above 0.1 SOC, the hysteresis (ΔV) is limited to 35-33 and 45-42 mV, for the relaxation of 5-120 min, respectively. Below 0.1 SOC, the ΔV_{error} with 5 min. relaxation is high, i.e., up to 200 mV for both cells. However, above 0.1 SOC this ΔV_{error} is approx. 16 mV and 7 mV for Li-Graphite and 1.5 mV and 0.5 mV for the Li-NMC cells, with 5 and 30 min. rest, respectively. The total experimental time required for the GITT test with 30 and 120 min. relaxations are ~2.7 and ~8.7 times longer compared to 5 min. relaxation for both the cells. In summary, the OCP and ΔV of the Li-Graphite cell are more sensitive to the relaxation duration compared to the Li-NMC cells. For a desired accuracy with reduced experimental duration for OCP and hysteresis measurement a variable rest duration is highly recommended with longer relaxation during the fast rate of change in voltage and shorter rest time in the voltage plateaus. The recommended relaxation for the Graphite and NMC electrodes are 30 min. and 5 min., respectively, beyond the 0.1 SOC. However, below 0.1 SOC at least 90 min. relaxation is appropriate to attain the accuracy of ~5mV for both of the electrodes.

Acknowledgement

This work was funded by the WMG centre High Value Manufacturing Catapult.

References

1. Y. Zhu, C. Wang, Strain accommodation and potential hysteresis of $LiFePO_4$ cathodes during lithium ion insertion/extraction, J. Power Sources, 196 (2011) 1442–1448.

2. W. Dreyer, J. Jamnik, C. Guhlke, R. Huth, J. Moškon, M. Gaberšček, The thermodynamic origin of hysteresis in insertion batteries, Nature Materials, 9 (2010) 448-453.
3. A. Barai, W.D. Widanage, J. Marco, A. McGordon, P. Jennings, A study of the open circuit voltage characterization technique and hysteresis assessment of lithium-ion cells, J. Power Sources, 295 (2015) 99-107.
4. M.A. Roscher, O. Bohlen, J. Vetter, OCV Hysteresis in Li-Ion batteries including two-phase transition materials, I. J. of Electrochem., 2011 (2011) 1-6.
5. G. Dong, J. Wei, C. Zhang, Z. Chen, Online state of charge estimation and open circuit voltage hysteresis modelling of $LiFePO_4$ battery using invariant imbedding method, Applied Energy, 162 (2016) 163–171.
6. M. Farkhondeh, C. Delacourt, Mathematical modelling of commercial $LiFePO_4$ electrodes based on variable solid-state diffusivity, J. Electrochem. Soc., 159 (2012) A177-A192.
7. F. Baronti, W. Zamboni, N. Femia, R. Roncella, R. Saletti, Experimental analysis of open-circuit voltage hysteresis in lithium-iron-phosphate batteries, IEEE Trans. (2013) 6728–6733.
8. J.E. Carrasco, A. Pe, S.A. Gómez, Hysteresis effect influence on electrochemical battery modelling, Electric Power Sys. Resarch, 152 (2017) 27–35.
9. F. Baronti, N. Femia, R. Saletti, W. Zamboni, Comparing open-circuit voltage hysteresis models for lithium-iron-phosphate batteries, IEEE Trans. (2014) 5635-5640.
10. J.R. Croy, K.G. Gallagher, M. Balasubramanian, B.R. Long, M.M. Thackeray, Quantifying hysteresis and voltage fade in $xLi_2MnO_3.(1\text{-}x)LiMn_{0.5}Ni_{0.5}O_2$ electrodes as a function of Li_2MnO_3 content, J. Electrochem. Soc., 161 (2014) A318–A325.

11. J.R. Croy, K.G. Gallagher, M. Balasubramanian, Z. Chen, Y. Ren, D. Kim, S. Kang, D.W. Dees, M.M. Thackeray, Examining hysteresis in composite $xLi_2MnO_3 \cdot (1-x)LiMO_2$ cathode structures, J. Phy. Chem., 117 (2013) 6525−6536.
12. M. Rashid, A. Sahoo, A. Gupta, Y. Sharma, Numerical modelling of transport limitations in lithium titanate anodes, Electrochim. Acta. 283 (2018) 313–326.
13. M. Rashid, A. Gupta, Experimental assessment and model development of cycling behaviour in Li-ion coin cells, Electrochim. Acta. 231 (2017) 171–184.
14. Y. Ji, R. Li, D. Mu, S. Sun, C. Dai, F. Ding, Surface modification of $Li_{1.2}Mn_{0.56}Ni_{0.16}Co_{0.08}O_2$ cathode material by supercritical CO_2 for lithium-ion batteries, J. Electrochem. Soc., 165 (2018) A2880–A2888.
15. S.R. Gowda, D.W. Dees, A.N. Jansen, K.G. Gallagher, Examining the electrochemical impedance at low states of charge in lithium- and manganese-rich layered transition-metal oxide electrodes, J. Electrochem. Soc., 162 (2015) 1374–1381.
16. Su-I1 Pyun , Y.-G. Ryu, Lithium transport though graphite electrodes that contain two stage phases, Journal of Power Sources, 70 (1998) 34–39.
17. Z. Shen, L. Cao, C.D. Rahn, C. Wang, Least squares galvanostatic intermittent titration technique (LS-GITT) for accurate solid phase diffusivity measurement, J. Electrochem. Soc., 160 (2013) 1842–1846.
18. S. Jin, J. Li, Z. Du, C. Daniel, D.L. Wood, Fast formation cycling for lithium ion batteries, J. Power Sources. 342 (2017) 846–852.
19. T. Spila, S.E. Trask, D.J. Miller, J.A. Gilbert, B.J. Polzin, A.N. Jansen, D.P. Abraham, Cycling behaviour of NCM523/Graphite lithium-ion cells in the 3–4.4 V range: diagnostic studies of full cells and harvested electrodes, J. Electrochem. Soc., 164 (2017) 6054–6065.

20. T.S. Pathan, M. Rashid, M. Walker, W.D. Widanage, E. Kendrick, Active formation of li-ion batteries and its effect on cycle life, J. Phys. Energy (in press): https://doi.org/10.1088/2515-7655/ab2e92
21. M. Rashid, A. Gupta, Effect of relaxation periods over cycling performance of a Li-ion battery, J. Electrochem. Soc. 162 (2015) A3145–A3153.
22. W. Lu, Q. Wu, D.W. Dees, Electrochemical characterization of lithium and manganese rich composite material for lithium ion batteries, J. Electrochem. Soc., 160 (2013) 950–954.